



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

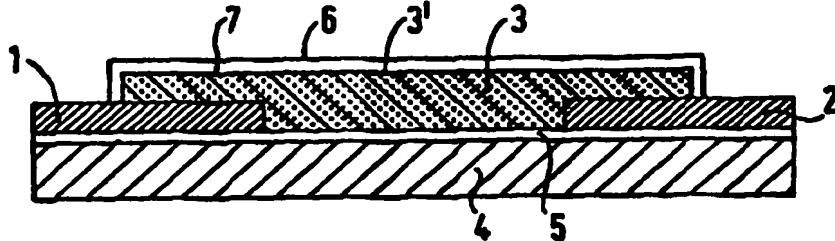
(51) International Patent Classification ⁶ : H01L 51/00	A2	(11) International Publication Number: WO 95/31833 (43) International Publication Date: 23 November 1995 (23.11.95)
(21) International Application Number: PCT/IB95/00346 (22) International Filing Date: 10 May 1995 (10.05.95) (30) Priority Data: 94201368.1 16 May 1994 (16.05.94) EP (34) Countries for which the regional or international application was filed: NL et al.		(81) Designated States: CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(71) Applicant: PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). (71) Applicant (for SE only): PHILIPS NORDEN AB [SE/SE]; Kottbygatan 5, Kista, S-164 85 Stockholm (SE). (72) Inventors: BROWN, Adam, Richard; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). DE LEEUW, Dagobert, Michel; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). LOUS, Erik, Jan; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). HAVINGA, Edsko, Enno; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). (74) Agent: TANGENA, Antonius, Gerardus; Internationaal Ocroibureau B.V., P.O. Box 220, NL-5600 AE Eindhoven (NL).		

(54) Title: SEMICONDUCTOR DEVICE PROVIDED WITH AN ORGANIC SEMICONDUCTOR MATERIAL

(57) Abstract

The invention relates to a semiconductor device provided with an organic material which is formed by a solid-state mixture of organic donor and organic acceptor molecules. A semiconducting solid-state mixture is known with molar ratios between donor and acceptor molecules of 1.3:2 and 1.66:2. The known solid-state mixture has the disadvantage that its electrical conductivity is comparatively high, so that it is not

possible to manufacture switchable devices from the mixture. According to the invention, the semiconductor device is characterized in that the material comprises an n- or p-type semiconductor material, the n-type semiconductor material having a molar ratio between the donor and acceptor molecules below 0.05, and the p-type semiconductor material having this ratio above 20. The solid-state mixtures according to the invention may be used for manufacturing switchable semiconductor devices. The n- and p-type organic solid-state mixtures can be used for manufacturing transistors, diodes, and field effect transistors in a same manner as, for example, doped silicon or germanium.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Semiconductor device provided with an organic semiconductor material.

The invention relates to a device provided with an organic material which is formed by a solid-state mixture of organic donor and organic acceptor molecules. "Donor molecule" is here understood to mean a molecule which can give off an electron comparatively easily, and "acceptor molecule" a molecule which can take up an electron
5 comparatively easily.

A solid-state mixture of the kind mentioned in the opening paragraph is known from European Patent Application no. 423956. The solid-state mixture is semiconducting at molar ratios between donor and acceptor molecules of 1.3:2 and 1.66:2. The known solid-state mixture described has the disadvantage that the electrical conductivity
10 of the known solid-state mixture is comparatively high, so that it is not possible to influence the conductivity of the solid-state mixture to the extent that switchable devices can be manufactured.

The invention has for its object *inter alia* to counteract this disadvantage.

According to the invention, the device is for this purpose characterized in
15 that the material comprises an n- or p-type semiconductor material, wherein the n-type semiconductor material has a molar ratio between the donor and acceptor molecules below 0.05, and wherein the p-type semiconductor material has this ratio greater than 20. It is accordingly possible with the donor/acceptor combination to manufacture an n-type as well as a p-type organic semiconductor.

20 The solid-state mixtures according to the invention may be used for manufacturing switchable semiconductor devices. The n- and p-materials may be used for manufacturing transistors, diodes, and field effect transistors in the same manner as, for example, doped silicon or germanium.

25 The known solid-state mixtures are used for manufacturing an organic conductor. Given a molar ratio between donor and acceptor molecules of 1:1, the solid-state mixture becomes semi-metallic. At donor/acceptor ratios of 1.3:2 and 1.66:2, i.e. comparatively close to 1:1, the conductivity of the solid-state mixture is lower than in the case of purely metallic conductivity. The conductivity is still so high that no switching elements can be made with the solid-state mixture. In addition, the known solid-state

mixtures do not exhibit n- or p-type behaviour, *i.e.* the conductivity is not determined by comparatively loosely bound electrons or holes. The solid-state mixture according to the invention, on the other hand, behaves as an n- or p-type semiconductor. This means that effects such as depletion, enhancement, injection of charge carriers, field effect, *etc.*, known

5 from other semiconductor materials, can be used for making switching elements.

The solid-state mixture behaves as an n-type semiconductor in the case of a molar solid-state mixture ratio between donors and acceptors below 0.05, *i.e.* with a relatively very large number of acceptor molecules. The solid-state mixture behaves as a p-type semiconductor in the case of a molar ratio above 20, *i.e.* with a relatively very large number of donor

10 molecules. In contrast to the mixture according to the invention, the presence of acceptor atoms leads to a p-type behaviour in semiconductor materials such as *e.g.* silicon, whereas the presence of donor atoms leads to an n-type behaviour.

It is suspected that the behaviour of the solid-state mixture with comparatively low and high molar donor/acceptor ratios is caused by a so-called hopping mechanism. Thus n-type behaviour of the solid-state mixture with a low molar donor/acceptor ratio could be caused by the fact that the conductivity is determined by electrons of donor molecules, of which there are relatively few, which move ("hop") to lattice locations (holes) on acceptor molecules, of which there are comparatively many available. The reverse could be the case for p-type material.

20 Preferably, the device comprises both an n-type region manufactured from the n-type material and a p-type region manufactured from the p-type material. The solid-state mixture used in a semiconductor device according to the invention may be manufactured comparatively easily through codeposition from two vapour sources, one for donor molecules and one for acceptor molecules, at a reduced pressure, for example lower than

25 $1.3 \times 10^{-3} \text{ N/m}^2$ (10^{-5} torr). The molar donor/acceptor ratio may be changed comparatively easily in that the yields of the sources are adapted, for example by adapting a source temperature. Thus both n-type and p-type regions of the organic semiconductor can be made in one vapour deposition process. The semiconductor device according to the invention, accordingly, is much easier to manufacture than, for example, silicon semiconductor devices

30 where high-temperature diffusion plays a part in manufacturing n- and p-type regions.

Preferably, the device comprises a pn junction between the p- and the n-type regions. Such a pn junction behaves as a diode and is a basic form of a switching element. The pn junction can also be manufactured in a simple manner, as can the separate p- and n-type regions, through variation of the yields of vapour deposition sources of donor and acceptor molecules.

An additional advantage is obtained when the device comprises a further region manufactured from a solid-state mixture of the organic donor and organic acceptor molecules, where the molar ratio between the donor and acceptor molecules is substantially equal to one. Such a region has semi-metallic properties and may thus be used, for example,
5 as a connection region, buried conductor, or interconnection between semiconducting regions. Semi-metallic regions can be manufactured in one process step, along with n- and p-type regions, in that the molar donor-acceptor ratio is changed to approximately 1:1 during manufacture. An additional metallization step is necessary in the manufacture of such a conductive region in the case of semiconductor materials such as silicon.

10 Preferably, the device comprises a region adjoining a surface and made from the n-type material provided with a passivated surface layer. It is found in practice that n-type material forms a passivating surface layer when it is exposed to air (a mixture of N₂ and O₂) after its manufacture under reduced pressure. If the semiconductor device is so manufactured that regions of n-type material adjoin a surface, then the device is passivated
15 after vapour deposition under vacuum conditions when it is exposed to an atmosphere containing oxygen. This effect may be compared to passivation of a silicon surface through formation of silicon dioxide.

20 Preferably, the device comprises a field effect transistor, with a source and a drain region, and with an interposed n-type channel region manufactured from the n-type material, which channel region is provided with a gate electrode which is separated from the channel region by an insulating layer, while a side of the channel region facing away from the gate electrode is provided with a passivated surface layer which adjoins a surface. The side of the channel region facing away from the gate electrode is passivated upon exposure to air. A comparatively narrow channel region results from this. Such a
25 narrow channel region has a favourable influence on a so-called on/off ratio of the field effect transistor, i.e. the difference in conductivity in the channel region when the channel is blocked or rendered conducting in known manner via the gate electrode.

Known donor molecules are, for example, TTF: tetrathiafulvalene, TMTTF: tetramethyltetrathiafulvalene, TSF: tetraselenafulvalene, TMTSF:
30 tetramethyltetrasilenafulvalene. Known acceptor molecules are, for example, TCNQ: tetracyanoquinodimethane, TNAP: tetracyanonaphthoquinodimethane, and TCNDQ: tetracyanodiquinodimethane. All these molecules can be used as donor and acceptor molecules in a solid-state mixture according to the invention. For further examples of organic donor and acceptor molecules, the reader is referred to the book: "Organic Charge-Transfer

"Complexes" by R. Foster, Academic Press 1969, Table 1.1, pp. 5-11. Preferably, the organic donor molecule comprises TTF: tetrathiafulvalene and the organic acceptor molecule comprises TCNQ: tetracyanoquinodimethane. These materials are comparatively easily available and can be readily applied at a temperature below 200°C.

5 An additional advantage is obtained when a surface of the device is provided with a surface layer which seals the device off against oxygen. The stability of the solid-state mixture is increased thereby. Preferably, the surface layer comprises silicon monoxide. Silicon monoxide can be applied at a comparatively low temperature of approximately 200°C, so that the organic donor and acceptor molecules are not attacked.

10 The invention will be explained in more detail below by way of example with reference to the drawings, in which:

Fig. 1 shows the conductivity S as a function of the molar donor/acceptor ratio D/A of the solid-state mixture,

15 Fig. 2 shows a semiconductor device with a MOSFET transistor provided with an organic semiconductor material according to the invention,

Fig. 3 shows the current I_{sd} between source 1 and drain 2 of the semiconductor device of Fig. 1 as a function of the voltage V_g at the gate electrode 4,

20 Fig. 4 shows the semiconductor device with an MIS diode provided with an organic semiconductor material according to the invention,

Fig. 5 shows the differential capacitance dQ/dV , Q being the charge at electrodes 4, 8 and V the voltage V_g at the gate electrode 4 of the semiconductor device of Fig. 4, as a function of the voltage V_g at the gate electrode 4, and

25 Fig. 6 shows the semiconductor device with a diode provided with a pn junction made of organic semiconductor material according to the invention.

The Figures are purely diagrammatic and not drawn to scale.

Corresponding parts have been generally given the same reference numerals in the Figures.

30 Figs. 2, 4 and 6 show semiconductor devices provided with an organic semiconductor material formed by a solid-state mixture of organic donor and organic acceptor molecules. A donor molecule is here understood to be a molecule which can give off an electron comparatively easily, and an acceptor molecule is understood to be a molecule which can take up an electron comparatively easily.

Known semiconducting solid-state mixtures have molar ratios between

donor and acceptor molecules of 1.3:2 and 1.66:2. Such solid-state mixtures have the disadvantage that the electrical conductivity is comparatively high, so that it is not possible to manufacture switchable devices with the mixture.

According to the invention, the semiconductor material comprises an n- or p-type semiconductor material such that the n-type material has a molar ratio between the donor and acceptor molecules below 0.05, and the p-type material has this ratio above 20. The solid-state mixture behaves as an n-type semiconductor when it has a molar ratio between donors and acceptors below 0.05, so with a relative very great number of acceptor molecules. The solid-state mixture behaves as a p-type conductor at a molar ratio above 20, so with a relative very large number of donor molecules.

Fig. 1 shows how the conductivity S varies as a function of the molar donor/acceptor ratio D/A in an n-type semiconductor material manufactured from TCNQ as the acceptor molecule and TTF as the donor molecule. The electrical conductivity can accordingly be varied over many orders of magnitude in that the molar ratio between donor and acceptor molecules is controlled. Fig. 1 shows that the mixtures according to the invention have an electrical conductivity which differs very strongly from semi-metallic conductivity such as is found for known solid-state mixtures with a molar donor/acceptor ratio D/A of approximately 1.

Fig. 2 shows a field effect transistor with a source region 1, a drain region 2 and an interposed n-type channel region 3 made from the n-type material, the channel region 3 being provided with a gate electrode 4 which is separated from the channel region 3 by an insulating layer 5, while a side 3' of the channel region 3 facing away from the gate electrode 4 is provided with a passivated surface layer 7 which adjoins a surface 6. Such a device is manufactured as follows. A strongly doped p-type silicon slice (approximately 0.02 Ωcm) is used as the gate electrode 4. On this slice, a 50 nm thick silicon dioxide layer is grown thermally in known manner as the insulating layer 5. On this insulating layer 5 a source region 1 and drain region 2 are formed from a vapour-deposited gold layer of approximately 0.1 μ thickness, which is patterned in known manner by photolithography and an etching process. The distance between the source and drain regions, the channel length L, is 5 μm, while the channel width Z, i.e. the width of the channel region 3 transverse to the plane of drawing, is 10 mm. The electrical resistance between source 1/drain 2 and the gate electrode 4 is more than 10¹² Ω here. Then a solid-state mixture is provided on the insulating layer 5 and on the source and drain regions 1, 2. The silicon slice is for this purpose placed in a vapourizing bell jar where a solid-state mixture of donor and acceptor molecules, TTF and TCNQ, respectively, in a molar ratio of approximately

1:200 is provided to a thickness of 0.17 μm at a pressure of $1.3 \times 10^{-4}\text{N/m}^2$ (1×10^{-6} torr). The TCNQ and TTF are provided from different vapour sources which are kept at a temperature of approximately 150°C. The electrical conductivity of the solid-state mixture applied is $5 \times 10^{-6} \text{ Scm}^{-1}$. The side 3' of the channel region 3 facing away from the gate electrode 4 is passivated upon exposure of the channel region 3 to air during the removal from the bell jar. The device according to the invention then comprises a channel region 3 made of n-type semiconductor material of the solid-state mixture provided with a passivated surface layer 7. It is found in practice that n-type material 3 forms a passivating surface layer 7 of approximately 0.15 μm when it is exposed to an atmosphere containing oxygen after its manufacture in vacuum. The oxygen renders the n-type solid-state mixture more insulating. This effect is strongest at a boundary surface between n-type mixture and the atmosphere and becomes progressively less so towards the bulk of the solid-state mixture. A comparatively shallow channel region 3 is created by this passivation. Such a shallow channel region 3 favourably affects a so-called on/off ratio of the field effect transistor, i.e. there is a great difference in conductivity in the channel region 3 when the channel is blocked in known manner via the gate electrode 4 and when the channel is made conducting. The conductivity of the channel region in the conducting state does decrease owing to the passivation because the channel region 3 becomes shallower (less thick). Fig. 3 is a graph in which a current I_{sd} between source 1 and drain 2 is plotted horizontally and a voltage V_g applied to the gate electrode 4 is plotted horizontally. The voltage between source 1 and drain 2 was set for a fixed value of 20 V here. The curve of Fig. 3 was registered 47 days after manufacture, so with a fully passivated surface. It is evident from Fig. 3 that the on/off ratio (measured for V_g of +20 and -20 V) is great: $3 \times 10^7/10^9$, i.e. approximately 300.

Fig. 4 shows a so-called MIS (Metal Insulator Semiconductor) diode according to the invention. This MIS diode is manufactured in a manner analogous to that of the field effect transistor of the preceding example, but no source and drain regions are provided now, whereas a second gold electrode 8 is provided on the surface 6. The MIS diode has a surface area of 0.31 mm^2 . The MIS diode behaves as a capacitance which can store charge Q at its electrodes 8 and 4. Fig. 5 shows a differential capacitance dQ/dV_g as a function of the voltage V_g applied to the gate electrode 4. Fig. 5 was registered at a frequency of 1 kHz and an amplitude of 0.5 V, the voltage V_g across the electrodes 4 and 8 being varied at a rate of 20 V/minute. The broken line 10 gives the differential capacitance of the device without the semiconductor layer 3, the full line 11 the differential capacitance of the device with the semiconductor layer 3. The differential capacitance value of curve 11

approaches the value of curve 10 for V_g greater than approximately 20 V. This indicates that the semiconductor material 3 is enhanced with electrons, so that the semiconductor region 3 is regarded as a conductor for the differential capacitance dQ/dV and the differential capacitance is determined by the insulating layer 5, as is the case for curve 10, where the 5 electrode 8 lies directly on the insulating layer. The differential capacitance value of curve 11 approaches that value of dQ/dV which belongs to an insulating layer comprising both the insulating layer 5 and the semiconductor region 3 when V_g becomes lower than approximately -20 V. This is an indication that the semiconductor region 3 is fully depleted of charge at these voltages. Fig. 5 shows clearly, therefore, that the solid-state mixture 10 behaves as an n-type semiconductor. It is noted that the MIS diode exhibits a hysteresis in its differential capacitance curve. The cause of this hysteresis is not clear, but it could be due to various mechanisms such as charge being held at a boundary surface, oxide charge, or migration of donor or acceptor molecules.

Fig. 6 shows a device which comprises both an n-type region 23 15 manufactured from the n-type material and a p-type region 22 manufactured from the p-type material, a pn junction 35 being formed between the p- and n-type regions. The device also comprises a further region 24 made from a solid-state mixture of the organic donor and organic acceptor molecules in which the molar ratio between the donor and acceptor molecules is substantially equal to one. The device of Fig. 6 is a diode. Such a device is 20 manufactured as follows. Solid-state mixtures of the donor and acceptor molecules are provided on an insulating substrate 20 made of glass. The silicon slice is for this purpose placed in a vapourizing bell jar where a solid-state mixture of TTF and TCNQ as the donor and acceptor materials, respectively, is provided from different vapour sources at a pressure of $1.3 \times 10^{-4} \text{ N/m}^2$ (1×10^{-6} torr). The temperatures of the vapour sources are set in 25 dependence on the desired ratio between donor and acceptor molecules. Different layers 21 to 24 are provided in one process sequence, i.e. without the substrate 20 being taken from the bell jar. First a semi-metallically conducting layer 21 comprising a solid-state mixture with a molar ratio TTF/TCNQ of approximately 1:1 is provided to a thickness of $0.2 \mu\text{m}$. This layer 21 acts as a first electrode of the semiconductor device. The electrical conductivity 30 of the solid-state mixture provided is approximately 1 Scm^{-1} . Then a p-type semiconductor layer 22 of $0.2 \mu\text{m}$ thickness is provided, comprising a solid-state mixture with a molar ratio TTF/TCNQ of approximately 200:1, without the substrate 20 being removed from the bell jar. The electrical conductivity of the solid-state mixture provided is $5 \times 10^6 \text{ Scm}^{-1}$. On the p-type layer 22, an n-type semiconductor layer 23 is provided, comprising a solid-state

mixture with a molar ratio TTF/TCNQ of approximately 1:200. The electrical conductivity of the solid-state mixture provided is 5×10^{-6} Scm⁻¹. On the n-type layer 23, a semi-metallic layer 24 is provided, comprising a solid-state mixture of the organic donor and the organic acceptor molecules, the molar ratio between the donor and acceptor molecules being

5 substantially equal to one here. A gold layer 25 of 0.2 μm thickness is provided on this semi-metallic layer 24 as a second electrode. The gold layer is shaped in known manner by vapour deposition, a photolithographical process, and etching. The organic layers 21 to 24 are then patterned by plasma etching. Subsequently, according to the invention, the surface 30 and the lateral sides of the device created by plasma etching are provided with a surface layer 26

10 which seals the device off against oxygen.

Such a layer is manufactured at a comparatively low temperature (200°C or lower) in a low-temperature CVD (Chemical Vapour Deposition) process. The layer seals the solid-state mixture off against oxygen, whereby the stability of the solid-state mixture increases.

15 Preferably, the surface layer 26 comprises silicon monoxide. Silicon monoxide can be provided in a known manner at a comparatively low temperature of approximately 200°C. The silicon monoxide layer ensures that the organic donor and acceptor molecules are not attacked.

Known donor molecules are, for example, TTF: tetrathiafulvalene, TMTTF: tetramethyltetrathiafulvalene, TSF: tetraselenafulvalene, TMTSF:

20 tetramethyltetraselenafulvalene. Known acceptor molecules are, for example, TCNQ: tetracyanoquinodimethane, TNAP: tetracyanonaphthoquinodimethane, and TCNDQ: tetracyanodiquinodimethane. All these molecules can be used as donor and acceptor molecules in a solid-state mixture according to the invention. The mention of the above donor and acceptor material is not to be regarded as limitative. Further examples of organic
25 donor and acceptor molecules can be found in the book: "Organic Charge-Transfer Complexes" by R. Foster, Academic Press 1969, Table 1.1, pp.5-11. A device according to the invention is also possible with donor and acceptor molecules other than those mentioned, for example, with the said donor or acceptor molecules which have in addition been provided with groups such as long carbon chains or benzene rings (macromolecules). Preferably, the
30 organic donor molecule comprises TTF: tetrathiafulvalene, and the organic acceptor molecule TCNQ: tetracyanoquinodimethane. These materials are comparatively easily available and can be readily applied at a temperature below 200°C.

The invention is not limited to the embodiments described above. The semiconductor device may comprise, instead of one switching element, many switching

elements on a common substrate. The semiconductor device may also comprise other switching elements such as, for example, bipolar transistors, diodes, field effect transistors, or thyristors. These devices are designed on the analogy of semiconductor devices known from silicon technology. The semiconductor devices may be made in that the solid-state mixture is patterned by known techniques such as photolithography and etching, for example, plasma etching. Conductive, p-type and n-type regions can be manufactured and shaped then by means of the solid-state mixture according to the invention.

Claims:

1. A semiconductor device provided with an organic material which is formed by a solid-state mixture of organic donor and organic acceptor molecules, characterized in that the material comprises an n- or p-type semiconductor material, wherein the n-type semiconductor material has a molar ratio between the donor and acceptor molecules below 0.05, and wherein the p-type semiconductor material has this ratio greater than 20.
2. A semiconductor device as claimed in Claim 1, characterized in that the device comprises both an n-type region manufactured from the n-type material and a p-type region manufactured from the p-type material.
3. A semiconductor device as claimed in Claim 2, characterized in that the device comprises a pn junction between the p- and the n-type regions.
4. A semiconductor device as claimed in Claim 1 in any one of the preceding Claims, characterized in that the device comprises a further region manufactured from a solid-state mixture of the organic donor and organic acceptor molecules where the molar ratio between the donor and acceptor molecules is substantially equal to one.
5. A semiconductor device as claimed in any one of the preceding Claims, characterized in that the device comprises a region adjoining a surface and made from the n-type material provided with a passivated surface layer.
6. A semiconductor device as claimed in any one of the preceding Claims, characterized in that the device comprises a field effect transistor, with a source and a drain region, and with an interposed n-type channel region manufactured from the n-type material, which channel region is provided with a gate electrode which is separated from the channel region by an insulating layer, while a side of the channel region facing away from the gate electrode is provided with a passivated surface layer which adjoins a surface.
7. A semiconductor device as claimed in any one of the preceding Claims, characterized in that the organic donor molecule comprises TTF: tetrathiafulvalene and the organic acceptor molecule comprises TCNQ: tetracyanoquinodimethane.
8. A semiconductor device as claimed in any one of the preceding Claims, characterized in that a surface of the device is provided with a surface layer which seals the

device off against oxygen.

9. A semiconductor device as claimed in Claim 8, characterized in that the surface layer comprises silicon monoxide.

1/3

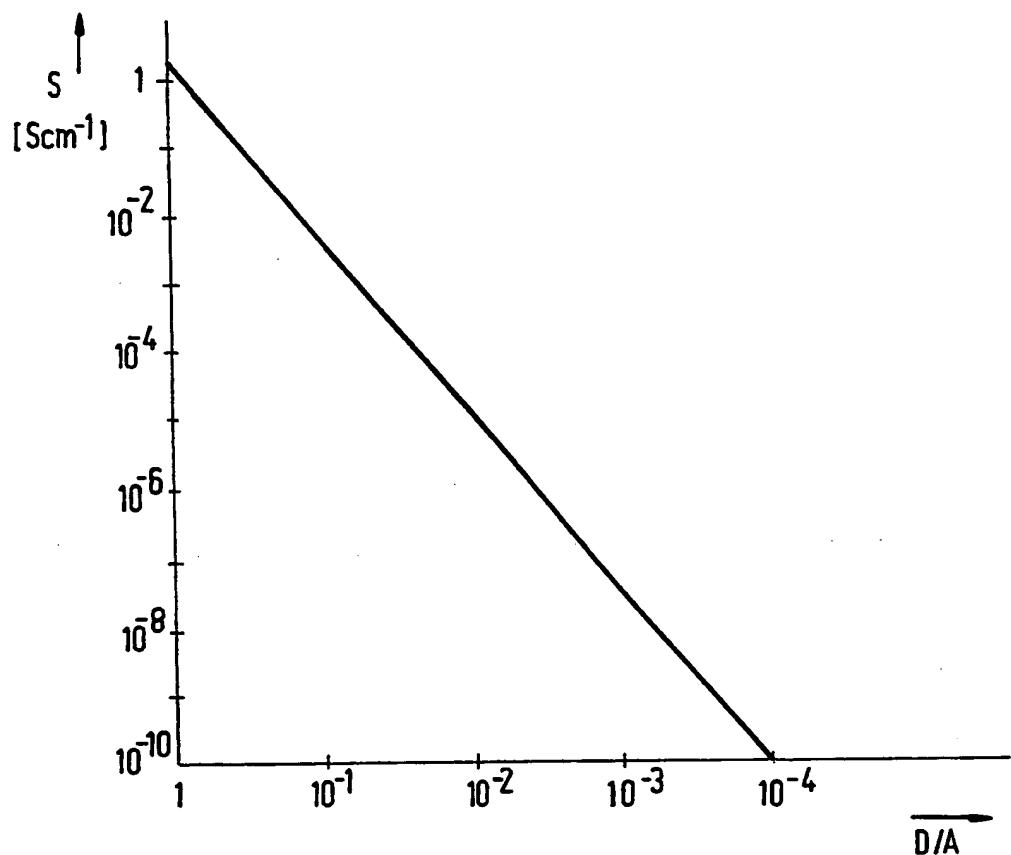


FIG.1

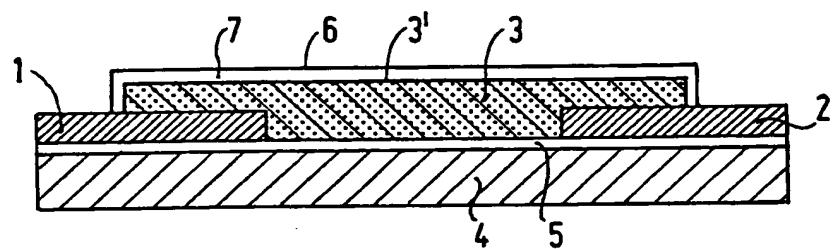


FIG.2

2/3

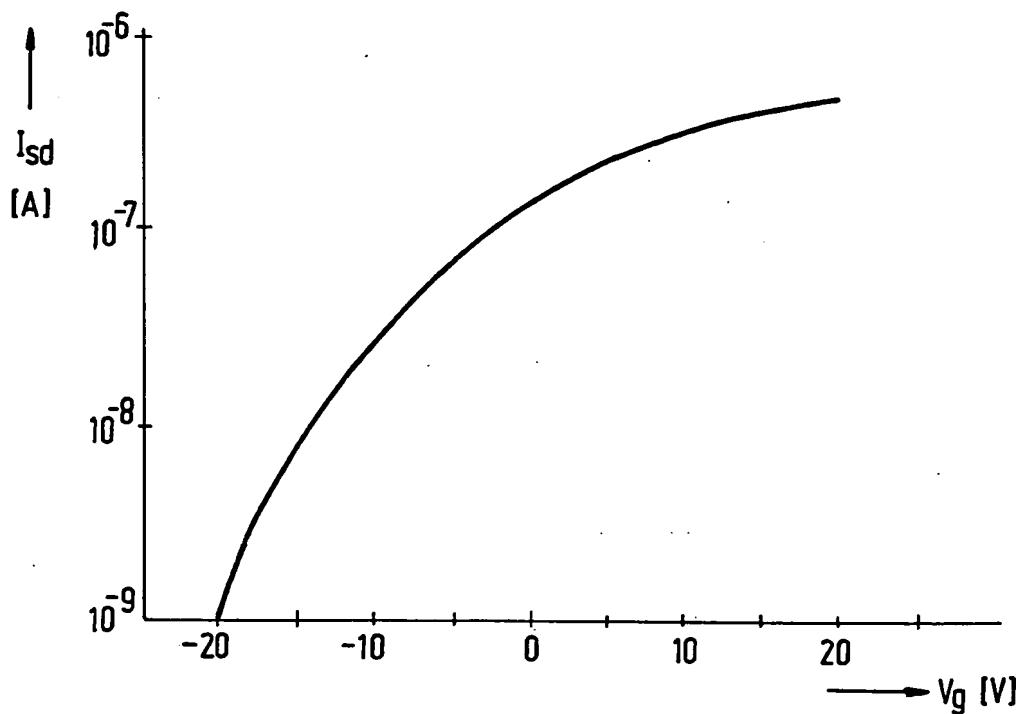


FIG.3

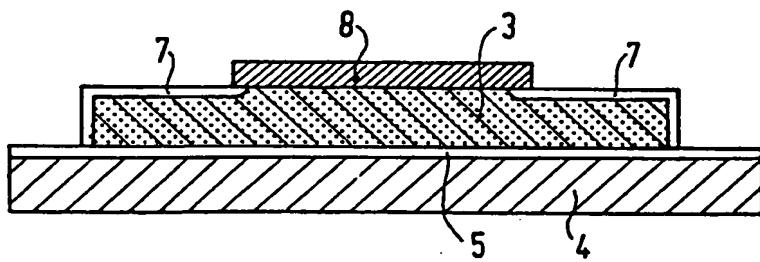


FIG.4

3/3

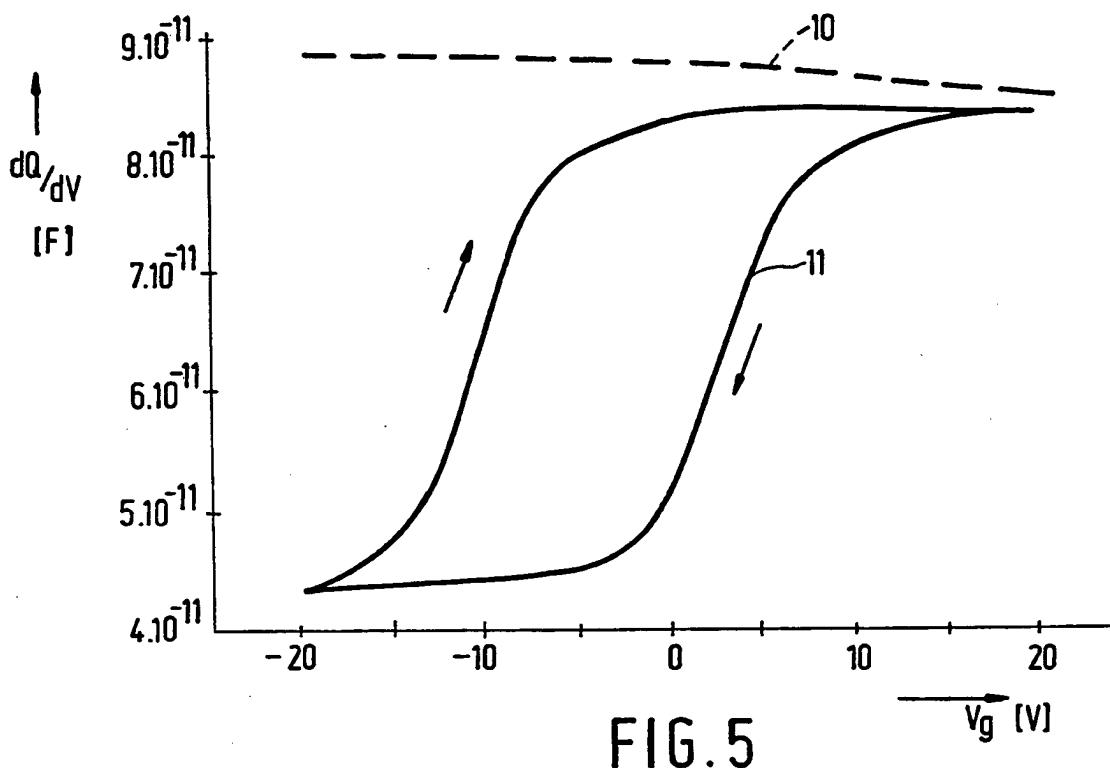


FIG. 5

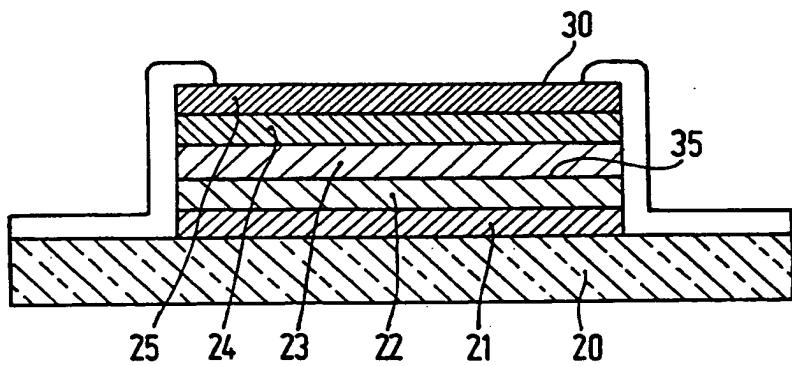
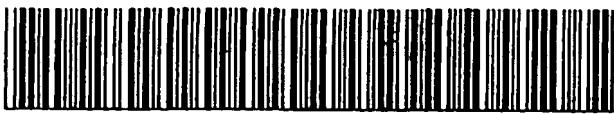


FIG. 6

PCT

WORLD INTELLECT
Inte

INTERNATIONAL APPLICATION PUBLISHING

(51) International Patent Classification⁶:

H01L 51/00, H01L 29/772 // H01B 1/12

WO 9531833A3

A:

(43) International Publication Date: 23 November 1995 (23.11.95)

(21) International Application Number: PCT/IB95/00346

(22) International Filing Date: 10 May 1995 (10.05.95)

(30) Priority Data:

94201368.1 16 May 1994 (16.05.94) EP
(34) Countries for which the regional or international application was filed: NL et al.

(81) Designated States: CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*(88) Date of publication of the international search report:
1 February 1996 (01.02.96)

(71) Applicant: PHILIPS ELECTRONICS N.V. [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).

(71) Applicant (for SE only): PHILIPS NORDEN AB [SE/SE]; Kottbygatan 5, Kista, S-164 85 Stockholm (SE).

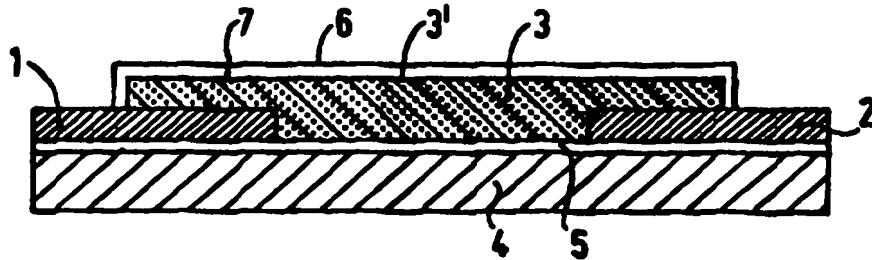
(72) Inventors: BROWN, Adam, Richard; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). DE LEEUW, Dagobert, Michel; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). LOUS, Erik, Jan; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL). HAVINGA, Edsko, Enno; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).

(74) Agent: TANGENA, Antonius, Gerardus; Internationaal Octroibureau B.V., P.O. Box 220, NL-5600 AE Eindhoven (NL).

(54) Title: SEMICONDUCTOR DEVICE PROVIDED WITH AN ORGANIC SEMICONDUCTOR MATERIAL

(57) Abstract

The invention relates to a semiconductor device provided with an organic material which is formed by a solid-state mixture of organic donor and organic acceptor molecules. A semiconducting solid-state mixture is known with molar ratios between donor and acceptor molecules of 1.3:2 and 1.66:2. The known solid-state mixture has the disadvantage that its electrical conductivity is comparatively high, so that it is not possible to manufacture switchable devices from the mixture. According to the invention, the semiconductor device is characterized in that the material comprises an n- or p-type semiconductor material, the n-type semiconductor material having a molar ratio between the donor and acceptor molecules below 0.05, and the p-type semiconductor material having this ratio above 20. The solid-state mixtures according to the invention may be used for manufacturing switchable semiconductor devices. The n- and p-type organic solid-state mixtures can be used for manufacturing transistors, diodes, and field effect transistors in a same manner as, for example, doped silicon or germanium.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 95/00346

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01L 51/00, H01L 29/772 // H01B 1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01L, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0592333 A1 (RHONE-POULENC FILMS), 13 April 1994 (13.04.94), page 2, line 49 - page 4, line 38, claim 1	1-3,5-8
A	page 2, line 49 - page 4, line 38 --	4
Y	US 4780790 A (K. TAKIMOTO ET AL), 25 October 1988 (25.10.88), column 6, line 34 - column 16, line 49; column 7, line 22 - column 12, line 31; column 16, line 65 - column 18, line 7, figures 5,9	1-3,5-8
A	column 6, line 34 - line 49; column 7, line 22 - column 12, line 31 --	4

 Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

21 December 1995

Date of mailing of the international search report

27 -12- 1995

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer

Stig Edhborg
Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 95/00346

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5238526 A (A. MIYANAGA ET AL), 24 August 1993 (24.08.93), column 1, line 6 - column 4, line 48 --	1-3,6-7
A	JP 2-282363 A (JAPAN CARLIT CO LTD), 19 November 1990 (19.11.90) --	1-3,5-8
A	US 4803011 A (A. BARRAUD ET AL), 7 February 1989 (07.02.89), column 3, line 12 - column 4, line 49 --	1-3
A	EP 0259040 A1 (HITACHI, LTD), 9 March 1988 (09.03.88), page 6, line 1 - line 13 -----	1-3

INTERNATIONAL SEARCH REPORT
Information on patent family members

11/12/95

International application No.	
PCT/IB 95/00346	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0592333	13/04/94	NONE		
US-A- 4780790	25/10/88	GB-A,B-	2190792	25/11/87
		GB-A-	2231201	07/11/90
		JP-A-	62271409	25/11/87
		JP-A-	62281460	07/12/87
		JP-A-	63033864	13/02/88
US-A- 5238526	24/08/93	EP-A-	0423956	24/04/91
		JP-A-	3173832	29/07/91
JP-A- 2-282363	19/11/90	NONE		
US-A- 4803011	07/02/89	DE-A-	3564055	01/09/88
		EP-A,B-	0165111	18/12/85
		FR-A,B-	2564231	15/11/85
		JP-C-	1782941	31/08/93
		JP-B-	4071591	16/11/92
		JP-A-	60243906	03/12/85
EP-A1- 0259040	09/03/88	JP-A-	63178110	22/07/88

THIS PAGE BLANK (USPTO)